

Transient photocurrent spectroscopy: Electrical detection of optical absorption for supported semiconductor nanocrystals in a simple device geometry

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The optical absorption of supported cadmium sulfide nanocrystals is directly detected as an electrical signal using a method described in this letter. Cadmium sulfide nanocrystals were epitaxially deposited onto highly oriented, pyrolytic graphite surfaces using a hybrid electrochemical/chemical synthesis method. The resulting submonolayer of cadmium sulfide nanocrystals was then covered with a thin (10–100 nm) insulating Formvar layer and a semitransparent gold top electrode. We exposed this structure to monochromatic chopped light and detected the transient photocurrent phase-sensitively and without applied bias. In the resulting device spectra, the absorption edge of the cadmium sulfide nanocrystals was clearly discernible at room temperature. The device response spectrum is compared with photoluminescence spectra acquired for the quantum dots in these devices at 20 K. © 1998 American Institute of Physics. [S0003-6951(98)02718-1]

Nanometer-sized semiconductor crystals [quantum dots (QDs)] have the potential to function as transducers for the conversion between optical and electrical signals in so-called “optoelectronic” devices. Optical to electrical transduction, however, requires that the absorption of light by QDs be detectable as an electrical signal. To our knowledge, there is just one published report of the electrical detection of optical processes in semiconductor QDs: Alivisatos and co-workers¹ have incorporated CdSe QDs into polymer thin film photovoltaic devices. In this letter, we demonstrate the feasibility of electrically detecting the absorption of light by a submonolayer coverage of cadmium sulfide QDs supported on a graphite surface.

Epitaxial cadmium sulfide QDs were synthesized using the “E/C” method as previously described.^{2,3} Briefly, cadmium nanocrystals were first electrochemically deposited on the graphite surface from an aqueous 1 mM Cd²⁺, 0.10 M NaF, plating solution using a deposition potential of –350 mV versus the reversible Nernst potential for cadmium metal in this solution. These Cd nanocrystals were then permitted to spontaneously oxidize to Cd(OH)₂ in the plating solution at open circuit for a few seconds and finally, OH[–] was displaced from the Cd(OH)₂ particles by exposure of these nanocrystals to 5 (v/v)% H₂S for 15 min at 300 °C.² The resulting nanocrystals have been characterized by transmission electron microscopy (TEM), selected area electron diffraction (SAED), x-ray photoelectron spectroscopy (XPS), and photoluminescence previously: The nanocrystals have the wurtzite crystal structure, are epitaxially aligned with the substrate, and oriented with their *c* axes perpendicular to the graphite surface as a result of an excellent lattice match between the hexagonal (0001) planes in the CdS NCs and the HOPG basal plane.² The mean size of

these CdS NCs have been measured using (TEM) and found to correlate well with the blue shift seen in photoluminescence spectra.²

The device structure shown in Fig. 1 was employed for photocurrent measurements of CdS QDs. These devices were constructed as follows: A 10–100 nm thick layer of the insulating polymer, Formvar, was deposited by first dissolving the Formvar in chloroform, then floating a few drops of this solution onto the surface of nanopure water in a beaker, and finally pulling the immersed graphite surface, on which CdS QDs had been deposited, through the floating polymer film. Following the evaporation of solvent from this film, a Scotch tape mask with a 5 mm diameter aperture was applied to the sample as a contact pad, then a thin semitransparent (10–15 nm) gold top electrode was evaporated onto the surface of the Scotch tape and the exposed Formvar film. After contacting this front electrode versus the graphite substrate, the

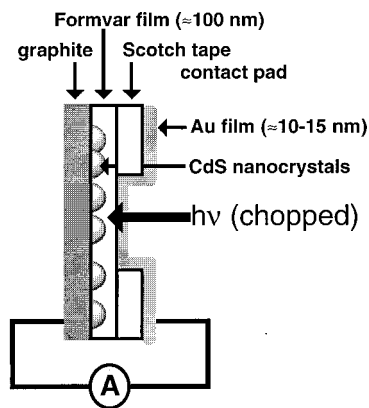


FIG. 1. Schematic diagram of the device structure for the transient photocurrent experiment. The “ammeter” consisted of a current amplifier followed by a lock-in amplifier which detected the current phase-sensitively. The monochromatized light was mechanically chopped.

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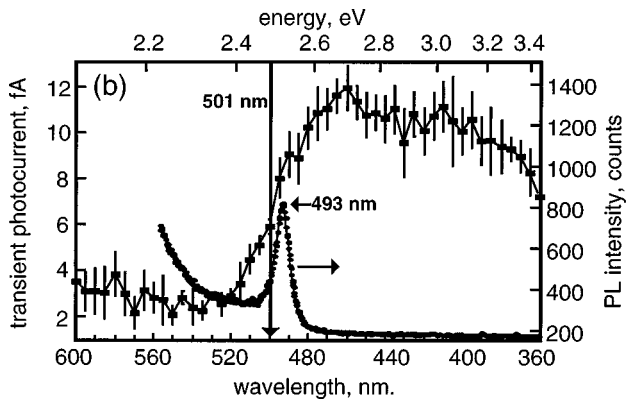


FIG. 2. Transient photocurrent spectrum for a device based on $r = 8$ nm CdS QDs supported on graphite surfaces at room temperature, and photoluminescence spectrum for the same device acquired at 20 K. The position of the absorption edge in the photocurrent spectrum is marked with a vertical arrow.

sample—shielded by a Faraday cage—was exposed to the chopped light of a 75 W Xe arc lamp, which was monochromatized using a 1/4 m monochromator (Oriel MS257) containing a 600 line/mm grating. Typical illumination intensities were 8 mW at 500 nm. The device current was amplified by a factor of 10^{10} V/A using a Keithley Model 428 current amplifier and phase-sensitively detected using an EG&G model 5210 lock-in amplifier at 300 μ V.

Prior to the construction of the device shown in Fig. 1, a photoluminescence (PL) spectrum for the CdS QDs was acquired: Freshly deposited CdS QDs on graphite were cooled to 20 K in a closed-cycle He cryostat, and exposed to the beam of an Ar⁺ laser emitting 150 mW at 351 nm. The fluorescence from the samples was collected by a Zeiss Epiplan LD 20 \times microscope objective, focused onto the entrance slit of an imaging spectrograph and dispersed onto a liquid-nitrogen-cooled CCD array with 1024 channels.

The transient photocurrent method which is employed here is similar to that variant of surface photovoltage spectroscopy (SPV) in which a fixed conductive probe is positioned close to a surface and the change in surface potential is measured synchronously with a light beam of oscillating intensity.⁴ In contrast to SPV, the photocurrent response is obtained when photoexcited electrons, produced in QDs supported on a conductive surface, are quenched by electron or hole transfer from the surface. The transfer of an electron, for example, from a QD to the graphite creates a positively charged particle on one plate of the capacitor; and the electron ends up on the other plate of the capacitor after passing through the ammeter. In other words, the change in surface potential is not directly detected as in SPV, instead the photocurrent resulting from the application of this potential difference to the impedance of the external circuit is measured in the absence of an applied bias. In terms of its polarity, the device photocurrent seen in these experiments corresponded to the transfer of photoelectrons from CdS quantum dots to the graphite surface.

Figure 2 shows room temperature transient photocurrent (“device”) spectra, and low-temperature PL spectra, for a device based on CdS nanocrystals having a radius of 8 nm (estimated from the energy of maximum emission). These CdS particles were prepared by depositing Cd metal using a

train of ten 20 ms voltage pulses—a tactic which we have shown improves the size monodispersity of CdS QDs.⁵ The resulting PL spectrum shows a slight blueshift of the emission maximum to 493 nm, corresponding to a particle radius of about 8 nm. This emission blueshift was found in about 60% of all areas sampled with the fluorescence microprobe and can thus be expected to appear in the transient photocurrent spectrum. This is indeed the case: The absorption edge is blueshifted to 501 nm proving that the photocurrent measurement is sensitive to the nanoparticle band gap even at room temperature. In contrast, PL spectra are virtually impossible to obtain under these conditions of sample temperature and particle areal density (typically 10^{10} cm⁻²). Control devices, with the construction shown in Fig. 1 but without QDs (i.e., using clean graphite surfaces) exhibited no photocurrent peaks above background.

The maximum photocurrent signal of 10×10^{-15} A can be translated into a maximum device quantum yield, ϕ_{device} (defined as the fraction of photoexcited QDs which contribute an electron to the externally measured device photocurrent): The illumination of a single semiconductor nanoparticle with a photon flux, N_{ph} , will yield a generation rate, g , for excited state electrons:

$$g = N_{ph} \sigma, \quad (1)$$

where σ is the absorption cross section of the particle. For semiconductor nanocrystals embedded in a medium having a refractive index, n_1 , and having a diameter, r , which is much smaller than the wavelength of light, Mie theory⁶⁻⁸ allows the value of σ to be estimated as follows:

$$\sigma = \frac{8 \pi^2 n_1}{\lambda} r^3 \text{Im} \left(\frac{m^2 - 1}{m^2 + 2} \right) \quad (2)$$

where m is given by

$$m = \frac{n_2 + i \frac{\alpha \lambda}{4 \pi}}{n_1}. \quad (3)$$

In Eq. (3), n_2 is the refractive index for the semiconductor and α its absorption coefficient ($\approx 10^4$ cm⁻¹). For $r = 80$ Å CdS ($n_2 = 2.32$) NCs embedded in Formvar ($n_1 \approx 1.5$), Eq. (2) gives $\sigma = 1.1 \times 10^{-14}$ cm². Equations (1) and 2 can then be used to calculate ϕ_{device} :

$$\phi_{\text{device}} = \frac{i_{\text{particle}}}{ge} = \frac{i_{\text{particle}}}{N_{ph} \sigma e}, \quad (4)$$

where e is the electron charge and i_{particle} is the device current per illuminated quantum dot (1.4×10^{-23} A particle⁻¹ for 10 fA total device current). For illumination conditions of 8 mW (at 400 nm), $N_{ph} = 2.3 \times 10^{17}$ s⁻¹ cm⁻², Eq. (4) yields $\phi_{\text{device}} = 3.4 \times 10^{-8}$.

In conclusion, transient photocurrent spectroscopy provides a means by which the absorption of light by semiconductor nanocrystals can be detected as an electrical signal. We have inadvertently shown that the sensitivity of the method is excellent. Devices based on just 2% of a monolayer of CdS nanocrystals (where each NC exhibits a quantum yield of $< 10^{-7}$) have produced photocurrent spectra having good signal-to-noise. Thus it is reasonable to assume that if radiative recombination can be suppressed and the

transfer of either photogenerated electrons or holes (but not both) to the conductive surface can be made faster, tremendous improvements in the sensitivity of these devices can be achieved. The transduction of optical absorption at QDs into electrical signals demonstrated here constitutes an important first step towards technological applications utilizing this interesting class of materials.

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